The role of phosphorus on eutrophication: a historical review and future perspectives

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Abstract

The eutrophication phenomenon is one of the main challenges regarding the ecological quality of surface waters, caused mainly by leaching of fertilizer from agriculture and by discharge of wastewater containing high amounts of phosphorus. This is a global environmental problem, which does not have yet a suitable solution. European Union developed and is implementing the Water Framework Directive (WFD-2000/60/EC), which requires the restoration of eutrophic water bodies quality until 2015; however, derogations have been claimed when eutrophication is the main pressure due to the complexity into recovery the degraded waters. In this context, this review aims to give a general overview of the historical evolution of phosphorus, its uses and consequently its role on eutrophication. Moreover, the main methodologies and some commercial products used for phosphorus precipitation are discussed. Since the main treatments focus on phosphorus precipitation, the scarcity of this mineral source is pointed out. More than an overview, this review leaves the question how many more years do we have enough mineral phosphorus reserves to guarantee enough food production.

Keywords: eutrophication; global situation; phosphorous removal; phosphorus scarcity

Phosphorus use

Since industrial revolution, the human population is growing and at the same time there is more demand for food supply. The use of fertilizers has became an imperative to answer the global food necessities. Phosphorus (P), which is removed from soil by crops, was replaced using waste products such as manure, crop residues and human excretes. The use of these methods allowed, at that time, to improve the agriculture fertility and maintain the level of crop production.[1-3]

In 1840, the German chemist Justus von Liebig demonstrated, for the first time, that the growth of terrestrial plants was conditioned by the nutrient in less quantity in the environment relative to the plant growth demand, his theory was termed as Liebig's Law of the Minimum.[4] The Liebig theory is contradictory to the humus theory, which was accepted until that time. This theory, very popular in the eighteenth century, defended that the organic compounds were the most important nutrients for plant growth. Fertilization with organic compounds was considered essential to improve the yield and the soil fertility. Liebig rejected this, demonstrating that only inorganic salts of P and nitrogen should be used as nutrient sources for plant growth, and he also considered that humus only gives CO_2 to be used by plants.[5] Therefore, he assumed that nutrients, such as, P , nitrogen and potassium, should be introduced into the soil to improve production.[3,5]

In the middle-to-late of nineteenth century, the increase in soil degradation and famines led Europe to search for new sources of fertilizers. The natural P biochemical cycle was interrupted (Figure 1), since it was no longer recycled. Guano (bird excreta rich in mineral P) was imported in Europe to be used as source of inorganic P. [1] The worldwide guano demand increased rapidly, which resulted in a decline in production by the end of nineteenth century. Since this became economically unfeasible, the P rock was seen as an unlimited source of concentrated P.[7] The fertilizers industry grew rapidly together with improvements in hygiene conditions. Human excreta was no longer used as soil fertilizers and was discharged into water bodies.

The use of fertilizers allowed a rapid replacement of P levels in soil, after the crops were harvested. The modern civilization changed from a P recycling society to a P throughput society. Since the sustainable cycle was interrupted, P was straightway moved from mines to oceans at levels much higher than the natural biogeochemical cycle, which takes tens of millions of years.[1] Rittmann et al. reported that the P content in worldwide fresh water systems increased at least 75% since pre-industrial revolution. The P fluxes went from 8 to 22 million metric tonnes per year in the same period. Therefore, P became an environmental pollutant in oceans, lakes and rivers waters.[8]

Eutrophication

As an effect of the P outflow to aquatic bodies, an over enrichment of nutrients occurred, which was defined as 'eutrophication'. Etymologically, 'eutrophic' means 'good

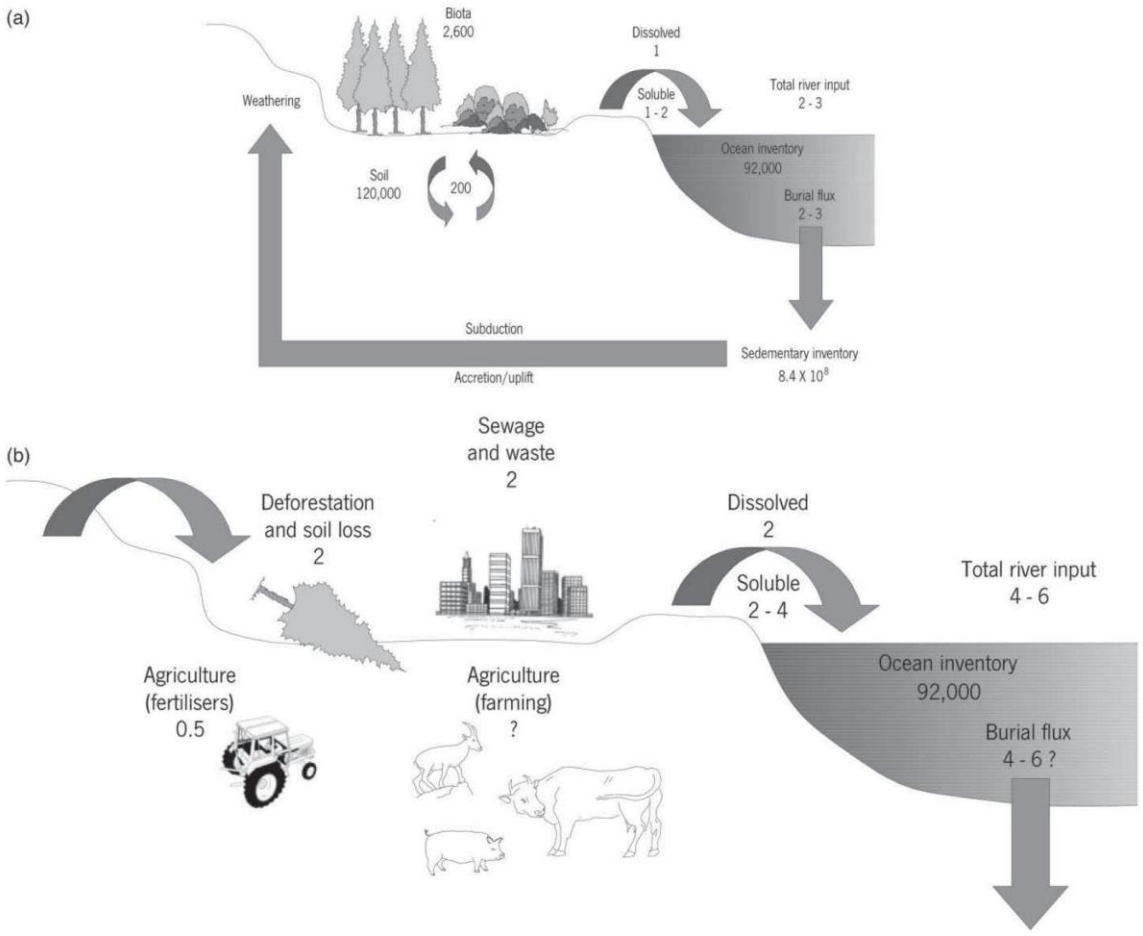

Figure 1. The dissolved phosphorus cycle (a) prior to human influence and (b) after human influence (adapted from Filippelli, 2002 [6]). Reservoir capacities in Tg phosphorus and fluxes indicated by arrows in Tg/ year phosphorus. nourishment', and eutrophication is the process by which water bodies grow in biomass productivity.[9] The term eutrophication was initially, 1919, applied in limnology by Naumann to provide a classification scheme according to plant production and nutrient available. Later, in 1929 Naumann transposed this classification on trophic degrees for water lakes types based on the production of organic matter by phytoplankton creating the oligotrophic-eutrophic paradigm (Figure 2).[10,11] The historical episodes of freshwaters eutrophication through Europe and North America are a reflex of the modern industrial society evolution. Ashley et al. enumerated a few cases, the Wisconsin lakes - Mendota and Monona in 1882, Lake of Zurich in 1896, Lake Erie in 1930 and Lake Washington in the 1950s.[5] Around 50 years ago it became clear that this good nourishment had tragic environmental effects in fresh waters environments, such as, rivers, dams and lakes. As a result of this concern, many political actions have been taken around the world, being expressed into programmes started by Coastal Zone Management Act (PL 92-583, 1972) and Clean Water Act (PL 92-500, 1972) in the USA, the Barcelona convention (MEDPOL) for the Mediterranean, legislative instruments for Urban Wastewater Treatment Directive (UWWTD-CEC, 1991a), Nitrates Directive (ND, CEC, 1991b), Helsinki Convention (HELCOM, 1994) for the Protection of Baltic Sea and OsloParis Convention for the Protection of Northeast Atlantic (OSPAR, 2002). Thus, at the end of the twentieth century, eutrophication had a scientific and legal meaning in Europe, and it was defined in OSPAR as:

> Eutrophication means the enrichment of water by nutrients causing an accelerated growth of algae and higher forms of plant life to produce an undesirable disturbance to the balance of organisms present in the water and to the quality of the water concerned, and therefore refers to the undesirable effects resulting from anthropogenic enrichment by nutrients.... [11]

To implement the reduction of nutrients level in fresh water environments, Europe developed more specific legislation described in the Water Framework Directive

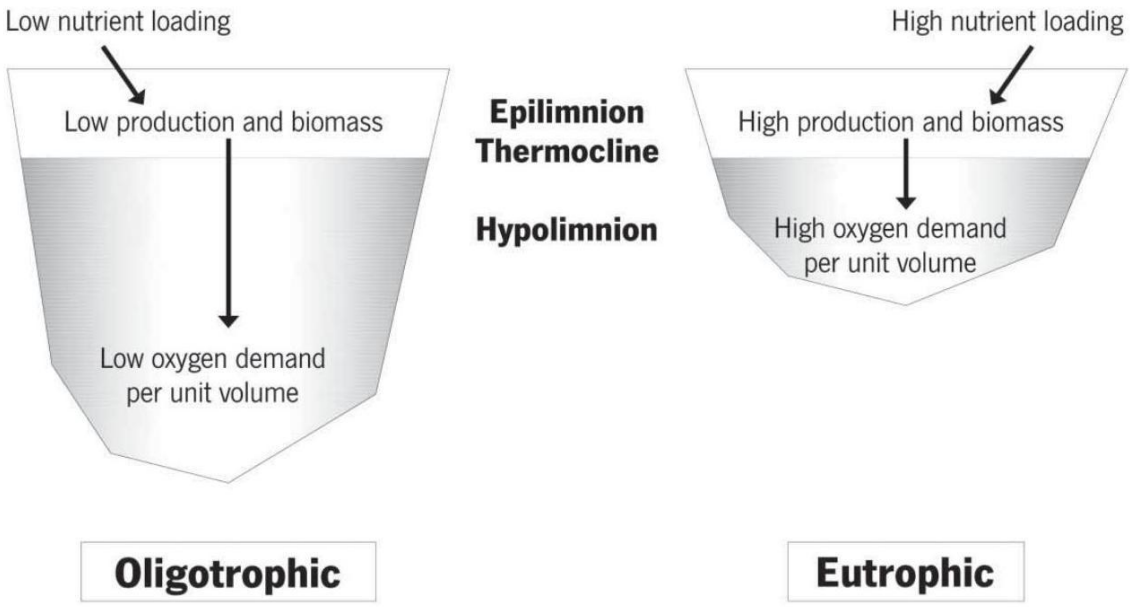

Figure 2. The oligotrophic-eutrophic paradigm (from Dokulil and Teubner [10]). (WFD-2000/60/EC) and in the Marine Strategy Framework Directive (MSFD-2008/56/EC), which established environmental policy for all European countries.

The MSFD Directive describes the negative effects that result from the eutrophication process: loss of biodiversity, ecosystem degradation, harmful algae blooms and oxygen deficiency in bottom waters. The abundance of algal blooms, often cyanobacteria, provokes a reduction of dissolve oxygen levels, which is one of the most common consequences. The depletion of oxygen can be high enough to create anoxia and consequently fish death, leading gradually to biodiversity reduction and creation of 'death zones'. As a result, more than 400 costal death zones were identified and this number increased by 10% per decade.[8] In severe cases, toxins might also be present in the water resulting from the domination of phytoplankton by bluegreen algae (cyanobacteria), where some of the produced compounds are more toxic than 'snake poison' making the water unsafe for consumption.[12-15] These serious problems have been reported in the literature for centuries, with narration of animal group death due to ingestion of large quantities of infested water. In the Bible (Exodus, 7: 2024), it is possible to read all the water of the Nile river became red as blood and fish which were in the river died. And the river was poisoned and the Egyptians could not drink its waters. In 1878, the first scientific report was published in Australia about domestic animals that had died as a consequence of poisoning after drinking water from lake Alexandrina, impaired by blue-green algae bloom. In 1988, Brazil dealt with 2000 gastroenteritis cases, which resulted in 88 deaths. The reason was a toxin produced by cyanobacteria (Anabaena and Microcystis) present in

the dam water used to supply the area.[16] Smol, in 1996, described the case of a farm near Baldur, Manitoba (Canada), where 16 cows were killed by nerve toxins from cyanobacteria blooming in a pond used for watering.[17] Dokulil and Teubner, 2011, summarized the principal consequences caused by eutrophication on watersheds as, increase in biomass of phytoplankton and macrophyte vegetation, shift to bloom-forming algal species that might be toxic or inedible, increase in biomass of benthic and epiphytic algae, change in species composition of macrophyte vegetation, increase in biomass of consumer species and incidence of fish kills, reduction in species diversity and in harvestable fish biomass, decrease in water transparency, oxygen depletion in the water body, taste, odour, and drinking water treatment problems, and decrease in perceived aesthetic value of the water body and pH variation.[10]

P sources

Concerning the P sources, these can be point or nonpoint (diffuse inputs into water bodies). While point sources are localized, easily monitored and controlled; nonpoint or diffuse sources are difficult to control and regulate and become important pollution channels.[18] Regarding the major sources of P , these are associated to high population density and correspondent sewage treated discharged and agriculture areas.[19-21] In the 1970s and 1980s, nonpoint sources were the main focus of concerned, since the reduction of point sources did not improve significantly the water quality. However, due to the complexity of the diffusion process, managing the risk of this P source is not straightforward, since variables, such as soil type, climate, topography, hydrology, land use and management can have a considerable effect.[18,22] Nevertheless, the relative contribution of this two P sources on eutrophic water varies from watershed to watershed.[3,23]

European situation

Examples of lakes, rivers and dams eutrophication are spread around the world. Meybeck in his studies indicated that streams and rivers have double nitrogen and

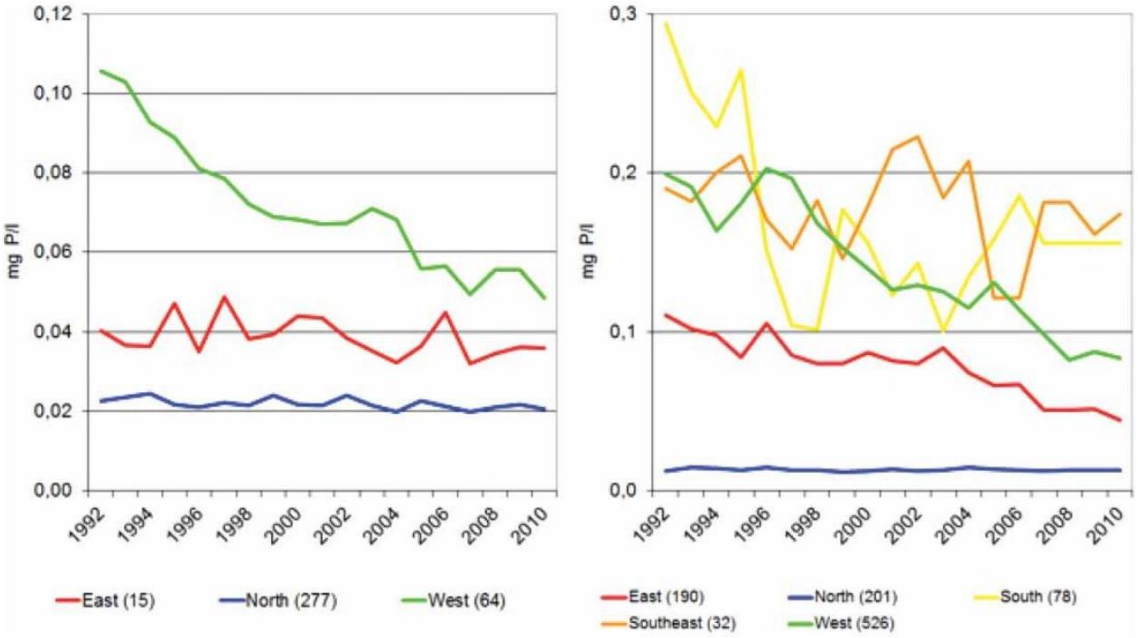

Figure 3. Concentration of phosphorus in rivers (left, ortophosphate) and lakes (right, total phosphorus) between 1992 and 2010 in different geographical regions of Europe.[27]

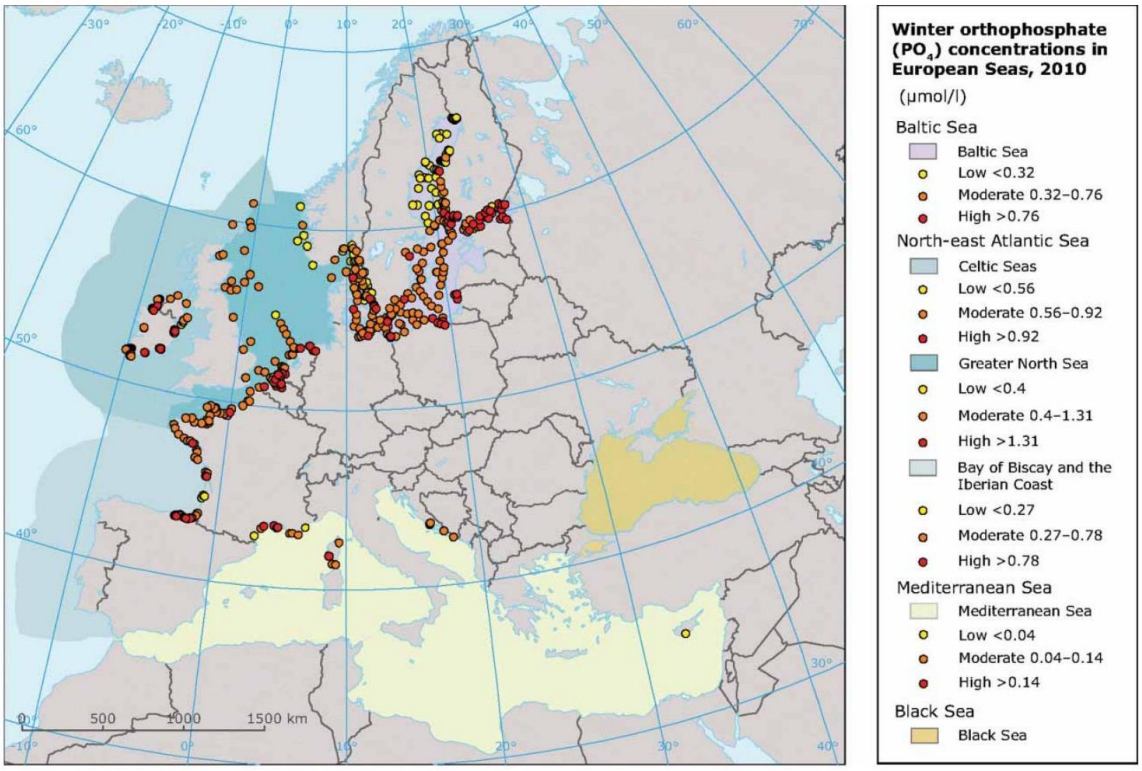

Figure 4. Winter orthophosphate concentrations in European seas in 2008.[28]

P concentrations worldwide, with local concentrations, sometimes, 50 times higher.[24,25] The Water Wheel reported that 54% of the lakes and reservoirs in Asia are

impaired by eutrophication, 53% in Europe, 48% in North America, 41% in South America and 28% in Africa.[26]

The European Environmental Agency (EEA) in a report from 2012 indicated that eutrophication of rivers and lakes is generally higher in central and southern Europeans countries and lower in the northern and alpines countries (Figure 3).[11,27] The European shore and marine waters were also target of assessment by EEA agency. The Waterbase CSI021 published in July 2011 identified the critical points in European seas (Figure 4).[28]

In the Baltic Sea, the highest P concentrations ($> 25\mu$ g/L) were registered at Finnish coastal stations in the Gulf of Finland and in Gulf of Riga. These high concentrations were motivated by internal P loading, which resulted from P released from bottom sediments during

Figure 5. Extensive surface blooms of cyanobacteria in 2005, Baltic Sea.[29] anoxic conditions.[28] As described by Voss et al., since the water has a long residence time, the Baltic Sea is especially sensible to nutrients inputs. Therefore, since 1950, visible nutrients loadings together with phytoplankton bloom have been witnessed, as depicted in Figure 5, where it is possible to see a cyanobacteria bloom.[30]

The highest P concentration ($> 100\mu$ g/L) was registered in the North Sea, in France and Belgium coastal waters. However, due to improvements on wastewater treatment, most of North Sea countries, a reduction of P loadings in 50%, between 1985 and 2005, resulted in a decrease of 28% of P concentration. [28,31]

The Mediterranean Sea exhibited low P concentration in the open sea; eutrophication was only observed in some costal waters. The highest P concentration ($> 30\mu$ g/L) was registered along western Italian coast.[28]

For Black Sea, no data concerning the winter nutrient concentrations in 2008 were submitted to the EEA. However, eutrophication effects have been noticed during the last 30 years (Figure 6). Between 1973 and 1990, it was estimated that five million tonnes of fish died as a consequence of eutrophication.

Methods to reduce/recuperate phosphorus in aquatic mediums

As explained above, eutrophication is a serious problem, therefore concerns about environmental sustainability are increasing, which are reflected by governmental policy and international agreements. The development of technologies

Figure 6. Satellite image of Black Sea algae bloom, captured in July 2010 by a camera on the European Space Agency's Envisat satellite.[32]
for P treatment started in 1950, aiming to reduce the amount that arrived in the waters surface. In the absence of a specific P removal step, during wastewater treatment, approximately 75% of the initial *P* load reaches the rivers.[33] Since P a non-renewable

resource, sewage treatment plants could be a potential source of P , capable of generating 15-20% phosphate rock world demand.[34] Nevertheless, the low P concentration (normally < 10mg/L) in wastewater streams

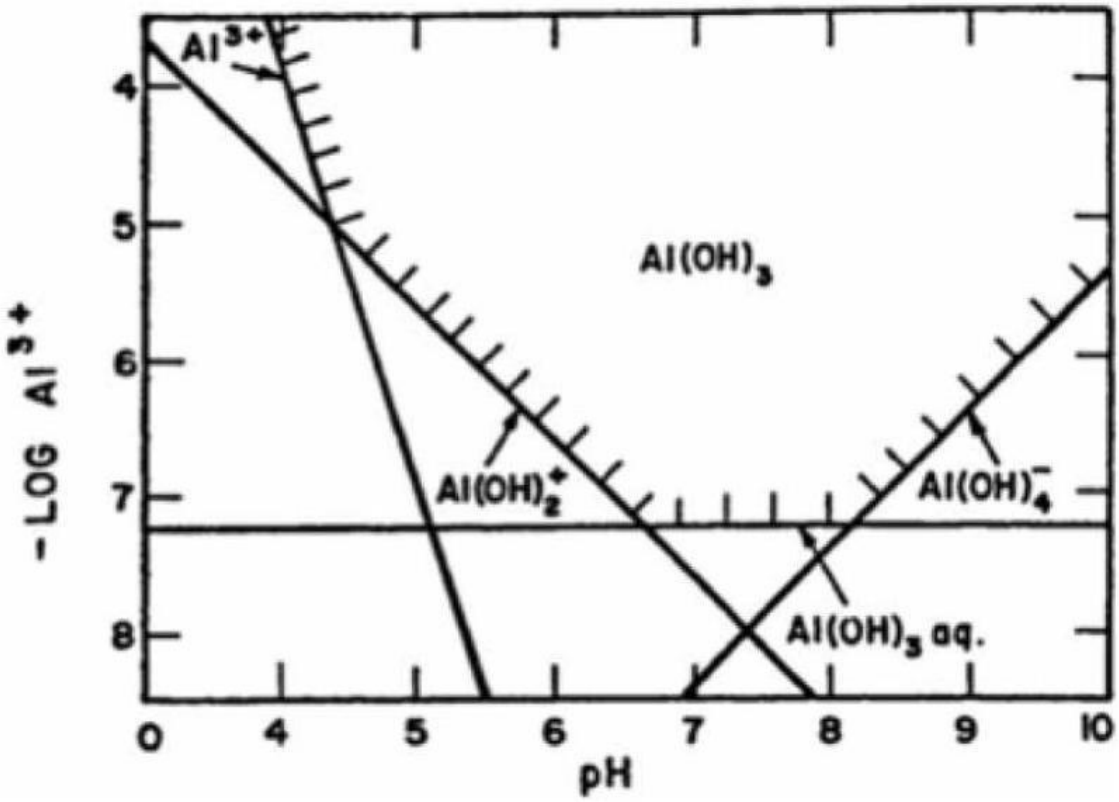

Figure 7. Solubility of aluminium hydroxide (from Miller [39]).
could turn the P recovery to an economically unfeasible process.

The most common P treatment process is based on chemical precipitation, which can be enhanced by biological adsorption or occasionally auto-precipitation (struvite).[35] While chemicals are able to treat P to lower levels, struvite formation requires higher concentrations of P , nitrogen and magnesium to occur.

Chemical P treatment

Nowadays, chemical precipitation is the main commercial process to treat P from eutrophic mediums and wastewater. It is based on the direct application of salts such as aluminium, iron or calcium, industrial by-products and mineral clays.[35-38] 2.3.1.1. Aluminium. The most common flocculation agent is aluminium sulphate (alum), which dissociates in water forming hydrated ions. The hydrolysis reaction in appropriated pH range gives aluminium hydroxide ($Al(OH)_3$) (Figure 7). Used both on wastewaters and natural waters, this is an amorphous flock with high coagulation capability and P adsorption properties, which precipitates *P* almost immediately.[40] When applied in a lake water treatment, it is critical to maintain the pH value in a tight range, which requires the use of buffers. Nevertheless in some lakes, where the pH is constant, an aluminium sediment capping could remain effective for at least 5 years or up to 20 years without a

new treatment.[41] The amount of aluminium to be used in the treatment depends on the concentration of reactive *P* and colloidal particles. From Equation (1), the stoichiometric indicates that alum and P molar ratio is 1: 2, where 0.87 kg of aluminium are able to remove 1 kg of P , if complete precipitation occurs[12,42]

$$Al_2(SO_4)_3 x H_2O + 2PO_4^{2-} \rightarrow 2AlPO_4 \downarrow + 3SO_4^{2-} + xH_2O \quad (1)$$

A large number of examples of aluminium application can be found in the literature.[43,44] Conover patented the use of aluminium hydroxide sulphate for water lake treatment. However, for pH values lower than 5.5 and higher than 8.0, the solubilization of aluminium phosphate occurred and the adsorbed *P* was released again to the water column.[45] Auvray et al. studied the use of alum on treatment of natural eutrophic waters and how the process was affected by the presence of algae and organic mater.[46] The total phosphorus removal efficiency reached $90 - 95\%$. Huang and Chiswell used air-dried spent alum to treat a wastewater effluent. A rapid P removal was detected and the P levels were reduced by 55% after 20 min of treatment, reaching an adsorption capacity of approximately $0.30 - 0.33$mg phosphate per 1 g of air-dried spent alum.[47]

The main disadvantages of the use of aluminium sulphate are the possibility of toxicity, pH reduction, low flock stability, demand to ensure dosage rate, smothering of benthos and a restriction period for drinking water, irrigation and stock watering. However, it has low cost, is applied in liquid form and the treatment cases are well documented.[39,42] Often, aluminium oxide is used to overcome these disadvantages.

Oliveira et al. proposed a different methodology able to treat and remove P , which is based on applying of polymer nanocomposite in eutrophic waters. These polymers contain very fine particles of aluminium oxide dispersed homogenously.[48] Designed to adsorb P on its surface, this nanocomposite allows *P* recovery, instead of promoting *P* precipitation and deposition at bottom of water medium. In the experiments performed, this material showed a removal rate of 0.8mgP/g.
2.3.1.2. Iron. Iron is generally applied as iron salts or as industrial by-products. It occurs in two different forms iron (II) and iron (III), the latter is more commonly used and the former has lower cost benefits resulting in an attractive alternative option.[47,49] Due to the chemical properties of the salt that can cause corrosion, staining, iron carryover and coloured, caution is necessary.[50] Depending on the physico-chemical parameters, when iron is applied to precipitate P , two different products can be obtained.[42,49]

$$Fe^{3+} + PO_4^{3-} \rightarrow FePO_4 \downarrow \quad (2)$$

$$3Fe^{2+} + 2PO_4^{3-} + 8H_2O \rightarrow Fe_3(PO_4)_2 \cdot 8H_2O \downarrow \quad (3)$$

The application of iron compounds to remove P requires always water aeration and pH control. According to Hickey and Gibbs, 1.8 kg of iron ion is required to remove 1 kg of P (Equation (3)). Since the addition of iron to lake water results in water pH reduction, buffers with low alkalinity are necessary.[42] In the bottom of the lakes, near the sediments, reduction conditions are predominant during hypolimnion seasonal stratification. The absence of oxygen results in the release of the P adsorbed, consequently microbial reduction of iron (III) to iron (II) occurs.[42] Regarding wastewater treatment, iron is mainly used as ferric chloride ($FeCl_3$). Theoretically 163.3 g of $FeCl_3$ reacts with 95 g of PO_4^{3-} to form 150.8 g of $FePO_4$. Nevertheless, experimental results demonstrated that a higher dosage of Fe^{3+} is necessary than the one predicted by $FePO_4$

stoichiometry, which can be explained by the competition between OH^-, colloids (e.g. dispersed microorganisms) and phosphate ions by Fe^{3+}.[50] In practice, the precipitate formed is a complex (Equation (4)). Then, the relationship between metal salt required and the P in solution is not stoichiometric. [33,51] Ferrous (Fe^{2+}) and ferric (Fe^{3+}) have different optimum pH ranges, ferric is between 4.5 and 5.0, and ferrous around 8, but for the last one good removal rates can be achieved from 7 to 8 . Since the reaction between ferrous and orthophosphate is practically instantaneous, properly mixing conditions are necessary to avoid the excess use of chemicals[52]

$$Fe^{3+} + yH_2O + xPO_4^{3-} \rightarrow Fe(OH)_y(PO_4)_x \downarrow + yH^+ \quad (4)$$

Boers and co-workers, in 1989, applied a daily dose of 100 g/m^2 of iron (III) to the sediments of eutrophic Lake Groot Vogelenzang in the Netherlands. The treatment was performed during two months, October and November. They registered a decrease in the total P and chlorophyll-a three weeks after finishing the treatment. However, three months later, the total P rose again[53]

Yamamoto-Ikemoto et al. studied the effect of iron coagulant on the control of filamentous bulking and phosphate removal. They found out that when $FeCl_2$ was added to the aeration tank, it successfully controlled the filamentous bulking and removed phosphate. Moreover, ferrous suppressed the phosphate release and sulphide production by waste sludge.[54]

2.3.1.3. Calcium. Among the three salts, calcium is the less commonly applied due to handling difficulties and large sludge production.[38,49] Limestone, which is a sedimentary rock composed of $CaCO_3$ (more than 50%) removes *P* according to the following equation:

$$10Ca^{2+} + 6PO_4^{3-} + 2OH^- \rightarrow Ca_{10}(PO_4)_6(OH)_2 \downarrow \quad (5)$$

The best pH range for the occurrence of this reaction is still under discussion, different ranges have been proposed (8.011.0, 7.5-8.5 or for $pH > 10.5$).[55] Karageorgiou et al. studied the removal of phosphorus species by adsorption onto calcite.[56] They concluded that the pH is the key variable on orthophosphate uptake, also, according to them, the process is more effective in the highly basic pH region.

The P removal with calcareous compounds induces an increase in water pH that might not be compatible with life in aquatic systems.[53] Moreover, literature studies reported that carbonate and phosphate ions compete for calcium, which inhibits the precipitation of calcium phosphate.[39,57] There are several examples worldwide where limestone has been used for P removal. In Melbourne, Australia, different grades of limestone were tested

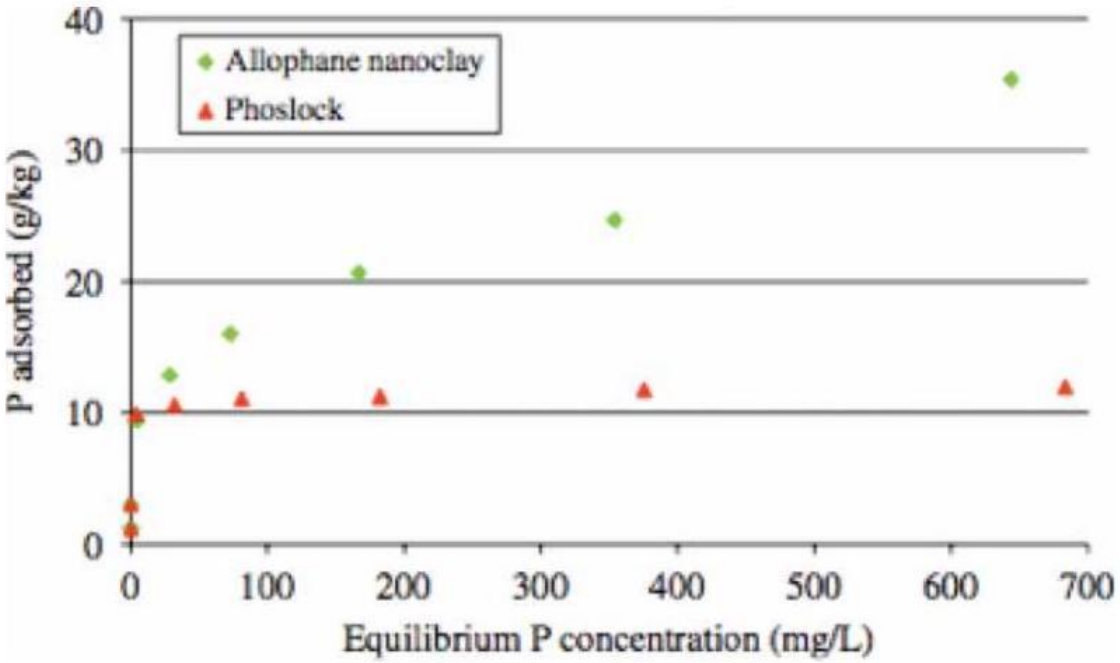

Figure 8. Phosphate adsorption isotherms on allophane nanoclay and Phoslock ™ (from Yuan and Wu [37]).

to reduce the P concentration in a small urban lake. The results indicated that only the fine grained was able to precipitate P.[39,57]

2.3.1.4. Mineral clays. As mineral clays are widely available in soil and sediments, they have been used as a flocculant and sorbent of suspended particles, diseasebearing organisms and toxic compounds in water and wastewater. Clays can be used in their natural form or after chemical treatment. The clays adsorption capability is due to its high specific surface area (external and internal), which extends to a few hundred m^2/g. Another important property is the presence of electrical charges of Al^{3+} and/or Si^{4+} that can be changed to adapt the surface charge to water pH change.[42]

Allophane is a group of mineral clays composed of alumina, silica and water. Results from vulwhichcanic ash materials, which has a large superficial are, they are highly porous with lower bulk density. Yuan and Wu in 2007 assessed the allophane capability to remove P from natural waters and compared it with Phoslock ™ (Figure 8). They showed that allophane was the sediment capping that allowed higher P removal.[37]

Wollastonite is a calcium metasilicate that is available all over the world and has been used as a secondary wastewater treatment of P sorption. Wollastonite removes P both by adsorption and precipitation mechanisms, but adsorption is usually faster than precipitation. Besides the good results obtained, some drawbacks were observed as a result of wastewater complexity.[55]

Alternative chemical compounds

Several waste products from industry have been used to substitute conventional chemicals. The most commonly used are alum residuals, red mud, fly ash, cement kiln dust and bone char, these are mainly composed of a significant fraction of divalent and trivalent ions as aluminium, iron and calcium.[8]

Oguz used blast furnace slag (BFS), a residual from steel-iron making process, to precipitate P.[58] BFS is composed of a mixture of metal oxides ($SiO_2$39.56%, $Al_2O_3$10.82% and CaO37.68%), removed around 99% of the phosphate from the solution. In spite of the high *P* adsorption capacity revealed in batch tests, the use of industrial by-products has serious limitations since they contain high concentrations of heavy metals that may contaminate the aquatic environment, increase water turbidity and pH. [59]

Filter mediums in artificial wetlands and infiltration plants for wastewater treatment are usually composed of industrial by-products, showing exceptional efficiency.[60] Nevertheless, the incorporation of such materials in the wetlands wastewater treatment is environmentally questionable.

Biological removal

Wetlands is the common way to perform biological P removal.[35] This low-cost and low-tech process has been used for decades to reduce the excess of nutrients present in domestic and industrial wastewater and agriculture runoffs, regarding the natural waters treatment, the first steps are being taken with the floating islands.[61] Wetlands are artificial ponds planted with aquatic and sometimes terrestrial plants.[35] The biggest difference between wetlands is the type of substract used for plants growth, which in some cases has also cleaning capacity (Figure 9). The variety of substrates includes, pumice, quartzite, light expanded clay aggregates, lightweight aggregates, wollastonite, shale, sand, maerl, zeolite, bauxite, synthetic hydrotalcite, BFS and fly ash.[61] In bottom of the wetlands, the plants' roots form an enormous biological filter. At the same time, microorganism that lives in submerged roots, degrade other pollutants, which are later absorbed by plants.

Commercial products

In the international market, some products are available to reduce the level of nutrients present in natural eutrophic

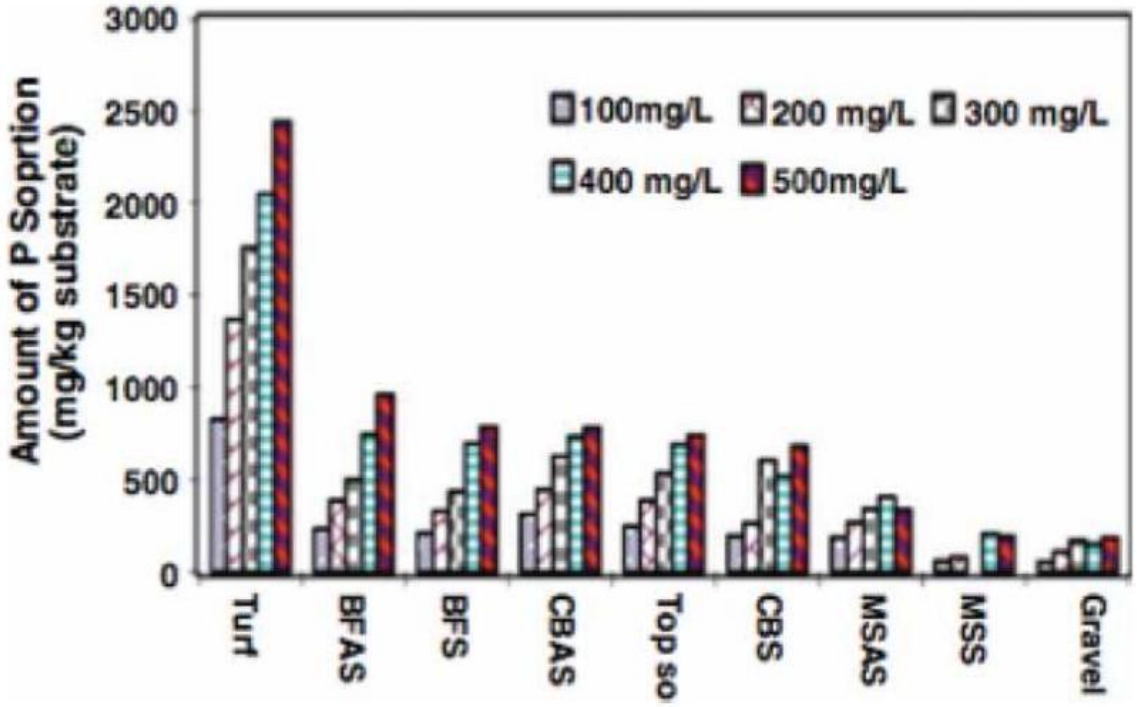

Figure 9. Amounts of P sorption by nine different substrate materials at five different initial P concentrations (from Cui et al. [61]). Blast furnace artificial slag (BFAS), BFS, coal burn artificial slag (CBAS), coal burn slag (CBS), midsized artificial sand (MSAS) and midsized sand (MSS).

waters. The next paragraphs make an overview about the two main commercial solutions with the principal properties described in Table 1. However, most of these commercial products only reduce the P concentration in aquatic medium, they do not recover it.

Plocher ™ is a product developed in 1980 by Roland Plocher. This was developed to stimulate the autoregeneration processes, promoting the rebalance of ecological and biological cycles. Plocher have been used in many countries in Europe, but better results were obtained in Switzerland (Heidsee lake), Germany (Gernshein lake), France (des Spains lake) and Austria (lake Oedt).[64,65] This product is protected by patent, thus there is no information available on the compositions. The accessible information describes Plocher as a material composed of cylindrical tubes containing aluminium, which can be applied directly in aquatic medium as powder or dispersed in solution.[65]

Phoslock ™ is a commercial product developed by Commonwealth Scientific and Industrial Research Organization, is based on bentonite clay with surface treatment, where

Table 1. Principal properties of Plocher and Phoslock.

	Advantages	Disadvantages	Mechanism

Plocher [62] Phoslock [35,63]	- Uses the self-cleaning power of water - Organic compounds are split up in H_2O, CO_2 and minerals - Supports plant growth to encourage spawning - Application either in granular or slurry - Rapid dispersion even in bed distribution - Not release phosphorus under anoxic conditions	- Not available - Partial smothering of benthos - Restriction period for drinking water, irrigation and stock watering - Sediment recovery reduces the efficiency - Slower action and reduce uptake at high pH	- Not available

sodium and calcium ions were changed by lanthanum.[63] P is removed by precipitation with lanthanum giving lanthanum phosphate. According to Equation (6), 1 kg of P requires 4.5 kg of lanthanum

$$La^{3+} + PO_4^{3-} \rightarrow LaPO_4 \downarrow \quad (6)$$

Phoslock ^{TM} is dispersed in a granular form with $1 - 3$ mm directly on the aquatic medium; it stays on the bottom, near the sediments.[35,63]

Phosphorus scarcity and future perspectives

While the research for efficient ways to control eutrophication is still in progress, a newer and serious concern is the depletion of mineral phosphate rock. Phosphorus (P) is an essential element for life.[2] Moreover, as a key element on fertilizers to improve the crop productions, P cannot be substituted, as described in 1974 by Isaac Asimov:

> We may be able to substitute nuclear power for coal, and plastics for wood, and yeast for meat, and friendliness for isolation-but for phosphorus there is neither substitute nor replacement. (Asimov, 1974 [66])

Also, the European Commission in Landfill Waste Directive of 1999 encourages a sustainable society where renewable resources should substitute non-renewable resources wherever it is possible. In cases where this cannot occur, recovery, reuse and recycling should be in practice.[67] Many scientists have been advertising P scarcity. It is expected that world population population reach nine billion people in 2050, thus assures enough *P* to guarantee the food production will be critical. The International Water Management Institute points out an increase of 70% of food production by 2050 to face the global demand.

At the moment, the main source of P is phosphate rock, a non-renewable source, which is becoming scarce and expensive. Described in Prud'homme [68], around 90% of phosphate is for food production, 82% being used in fertilizers, 7% for animal feed and $1 - 2$% for

food additives. Accepted and recognized by fertilizer industries, the reserves quality is declining and the cost of extraction, processing and shipping is increasing.[2,3]

As a non-renewable resource, a peak on phosphate rock production is expected around 2030-2040, if the current demand for fertilizers keeps constant. In 1949, Hubbert and later other scientists claimed that the critical period will be not when 100% of reserves will be minimal, but when the high-quality reserves will be depleted and the cost to reach a new high-quality reserves unfeasible.[2] Approximately 98% of world phosphate rock reserves are controlled by five countries, USA, Morocco and China being the most important.

Conclusions

Despite the achievements of P precipitation as an eutrophication treatment, little attention has been taken regarding recycling or recovery. Since P source is finite, to answer the global food demand for fertilizers, it is necessary to develop and implement new approaches and technologies that are able to recycle this essential nutrient. Eutrophic waters mediums and wastewaters should be seen as new generators of high-quality P sources. Therefore, treating eutrophic and wastewaters, to recover *P* as a valuable product that could be used in fertilizers, should be the main target. Nevertheless, this goal can only be achieved by research on technologies based on P adsorption, new supports, which allow P adsorption and desorption, methodologies to recover the charged adsorbent and efficient environmental-friendly regeneration treatments.

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References

[1] Ashley K, Cordell D, Mavinic D. A brief history of phosphorus: from the philosopher's stone to nutrient recovery and reuse. Chemosphere. 2011;84:737-746.
[2] Schröder JJ, Cordell D, Smit AL, Rosemarin A. Sustainable use of phosphorus report, EU, EU; 2009, p. 140.
[3] Cordell D, Drangert J-O, White S. The story of phosphorus: global food security and food for thought. Glob Environ Change. 2009;19:292-305.
[4] Smith VH, Tilman GD, Nekola JC. Eutrophication: impacts of excess nutrient inputs on freshwater, marine, and terrestrial ecosystems. Environ Pollut. 1999;100:179-196.
[5] Krasil'nikov NA. Soil microorganisms and higher plants. Soil Sci. 1963;95:285-296.
[6] Filippelli GM. The global phosphorus cycle. Rev Mineral Geochem. 2002;48:391-425.
[7] Schmid Neset TS, Bader HP, Scheidegger R, Lohm U. The flow of phosphorus in food production and consumption - Linkoping, Sweden, 1870-2000. Sci Total Environ. 2008;396:111-120.
[8] Rittmann BE, Mayer B, Westerhoff P, Edwards M. Capturing the lost phosphorus. Chemosphere. 2011;84:846-853.
[9] Kitsiou D, Karydis M. Coastal marine eutrophication assessment: a review on data

analysis. Environ Int. 2011;37:778801.
[10] Dokulil MT, Teubner K. Eutrophication and climate change: present situation and future scenarios. In: Ansari AA, Singh Gill S, Lanza GR, Rast W, editors. Eutrophication: causes, consequences and control. The Netherlands: Springer; 2011. p. 1-16.
[11] Ferreira JG, Andersen JH, Borja A, Bricker SB, Camp J, Cardoso da Silva M, Garcés E, Heiskanen A-S, Humborg C, Ignatiades L, Lancelot C, Menesguen A, Tett P, Hoepffner N, Claussen U. Overview of eutrophication indicators to assess environmental status within the European Marine Strategy Framework Directive. Estuar Coast Shelf Sci. 2011;93:117131.
[12] Yeoman S, Stephenson T, Lester JN, Perry R. The removal of phosphorus during wastewater treatment: a review. Environ Pollut. 1988;49:183-233.
[13] Correll D. Phosphorus: a rate limiting nutrient in surface waters. Poultry Sci. 1999;78:674-682.
[14] Skulberg OM, Codd GA, Carmichael WW. Toxic bluegreen algal blooms in Europe: a growing problem. Ambio. 1984;13:244-247.
[15] Carmichael WW. Toxic freshwater blue-green algae (cyanobacteria): an overlooked health threat. Health Environ Digest. 1991;5:1-4.
[16] Volterra L, Boualam M, Ménesguen A, Duguet JP, Duchemin J, Bonnefoy X. Eutrophication and health. Report from European Union and World Health Organization; 2002: 11-18.
[17] Smol JP. Eutrophication: the environmental consequences of over-fertilization. Oxford: Blackwell Publishing; 2008.
[18] Howden NJK, Bowes MJ, Clark ADJ, Humphries N, Neal C. Water quality, nutrients and the European union's Water Framework Directive in a lowland agricultural region: Suffolk, south-east England. Sci Total Environ. 2009;407:29662979.
[19] Bowes MJ, Leach DV, House WA. Seasonal nutrient dynamics in a chalk stream: the River Frome, Dorset, UK. Sci Total Environ. 2005;336:225-241.
[20] Neal C, Jarvie HP, Neal M, Love AJ, Hill L, Wickham H. Water quality of treated sewage effluent in a rural area of the upper Thames Basin, southern England, and the impacts of such effluents on riverine phosphorus concentrations. J Hydrol. 2005;304:103-117.
[21] Jarvie HP, Neal Colin, Withers PJA. Sewage-effluent phosphorus: a greater risk to river eutrophication than agricultural phosphorus? Kidlington, ROYAUME-UNI: Elsevier Kidlington; 2006.
[22] Heathwaite AL, Quinn PF, Hewett CJM. Modelling and managing critical source areas of diffuse pollution from agricultural land using flow connectivity simulation. J Hydrol. 2005;304:446-461.
[23] Mittelstet AR, Heeren DM, Fox GA, Storm DE, White MJ, Miller RB. Comparison of subsurface and surface runoff phosphorus transport rates in alluvial floodplains. Agric Ecosyst Environ. 2011;141:417-425.
[24] Meybeck M. Carbon, nitrogen and phosphorus transport by world rivers. Am J Sci. 1982;282:401-450.
[25] Meybeck M. Global analysis of river systems: from Earth system controls to Anthropocene syndromes. Philos Trans R Soc Lond B Biol Sci. 2003;358:1935-1955.
[26] Nyenje PM, Foppen JW, Uhlenbrook S, Kulabako R, Muwanga A. Eutrophication and nutrient release in urban areas of sub-Saharan Africa - a review. Sci Total Environ. 2010;408:447-455.
[27] Nutrients in freshwater. CSI 20, EEA; 2012.
[28] Nutrients in transitional, coastal and marine waters. CSI 021, European Environment Agency - EEA; 2012.
[29] News B. Satellite spies vast algal bloom in Baltic Sea. London: BBC; 2010.

[30] Voss M, Dippner JW, Humborg C, Hürdler J, Korth F, Neumann T, Schernewski G, Venohr M. History and scenarios of future development of Baltic Sea eutrophication. Estuar Coast Shelf Sci. 2011;92:307-322.
[31] Commission O. Nutrient reduction scenarios for the north sea. Nutrient reduction scenarios for the North Sea. OSPAR ed.; 2008.
[32] SMHI. GES Distributed Active Center; 2005.
[33] Parsons SA, Smith JA. Phosphorus removal and recovery from municipal wastewaters. Elements. 2008;4:109-112.
[34] Yuan Z, Pratt S, Batstone DJ. Phosphorus recovery from wastewater through microbial processes. Curr Opin Biotechnol. 2012;23:878-883.
[35] de-Bashan LE, Bashan Y. Recent advances in removing phosphorus from wastewater and its future use as fertilizer (1997-2003). Water Res. 2004;38:4222-46.
[36] Morse GK, Brett SW, Guy JA, Lester JN. Review: phosphorus removal and recovery technologies. Sci Total Environ. 1998;212:69-81.
[37] Yuan G, Wu L. Allophane nanoclay for the removal of phosphorus in water and wastewater. Sci Technol Adv Mater. 2007;8:60-62.
[38] Yang K, Li Z, Zhang H, Qian J, Chen G. Municipal wastewater phosphorus removal by coagulation. Environ Technol. 2010;31:601-609.
[39] Miller N. Locally available adsorbing materials sediment sealing and flocculants for chemical remediation of lake and stream. Roturua: Analytical & Environmental Consultants; 2005. p. 82.
[40] Landis CR, Gray SR. Methods to making water treatment compositions and compositions thereof. United States application patent US. 2003, p. 5.
[41] Welch EB, Cooke GD. Effectiveness and longevity of phosphorus inactivation with alum. Lake Reservoir Manage. 1999;15:5-27.
[42] Hickey CW, Gibbs MM. Lake sediment phosphorus release management - decision support and risk assessment framework. New Zeal J Mar Freshwat Res. 2009;43:819-856.
[43] Paerl HW, Xu H, McCarthy MJ, Zhu G, Qin B, Li Y, Gardner WS. Controlling harmful cyanobacterial blooms in a hyper-eutrophic lake (Lake Taihu, China): the need for a dual nutrient (N & P) management strategy. Water Res. 2011;45:1973-1983.
[44] Miller ML, Bhadha JH, O'Connor GA, Jawitz JW, Mitchell J. Aluminum water treatment residuals as permeable reactive barrier sorbents to reduce phosphorus losses. Chemosphere. 2011;83:978-983.
[45] Conover BR. Method of treating lake water with aluminium hydroxide sulfate. United States patent US5039427 A. 1991. p. 4 .
[46] Auvray F, van Hullebusch ED, Deluchat V, Baudu M. Laboratory investigation of the phosphorus removal (SRP and TP) from eutrophic lake water treated with aluminium. Water Res. 2006;40:2713-2719.
[47] Huang S-H, Chiswell B. Phosphate removal from wastewater using spent alum sludge, Vol. 42, London, ROYAUME-UNI: International Water Association; 2000.
[48] Oliveira M, Machado AV, Nogueira R. Phosphorus removal from eutrophic waters with an aluminium hybrid nanocomposite. Water Air Soil Pollut. 2012;223:4831-4840.
[49] Clark T, Stephenson T, Pearce PA. Phosphorus removal by chemical precipitation in a biological aerated filter. Water Res. 1997;31:2557-2563.
[50] Valsami-Jones E. Phosphorus in environmental technologies: principles and applications. Wageninggen: International Water Assn; 2004.
[51] Fytianos K, Voudrias E, Raikos N. Modelling of phosphorus removal from aqueous and wastewater samples using ferric iron. Environ Pollut. 1998;101:123-130.
[52] Thistleton J, Berry TA, Pearce P, Parsons SA. Mechanisms of chemical phosphorus removal II: iron (III) salts. Process Saf Environ Prot. 2002;80:265-269.
[53] Gulati RD, van Donk E. Lakes in the Netherlands, their origin, eutrophication and

restoration: state-of-the-art review. Hydrobiologia. 2002;478:73-106.
[54] Yamamoto-Ikemoto R, Matsui S, Komori T, BosqueHamilton EK. Control of filamentous bulking and interactions among sulfur oxidation-reduction and iron oxidationreduction in activated sludge using an iron coagulant. Water Sci Technol. 1998;38:9-17.
[55] Johansson Westholm L. Substrates for phosphorus removalpotential benefits for on-site wastewater treatment? Water Res. 2006;40:23-36.
[56] Karageorgiou K, Paschalis M, Anastassakis GN. Removal of phosphate species from solution by adsorption onto calcite used as natural adsorbent. J Hazard Mater. 2007;139: 447-452.
[57] Drizo A, Frost CA, Grace J, Smith KA. Physical-chemical screening of phosphate removing substrates for use in constructed wetland systems. Water Res. 1999;33:3595-3602.
[58] Oguz E. Removal of phosphate from aqueous solution with blast furnace slag. J Hazard Mater. 2004;114:131-137.
[59] Ballantine DJ, Tanner CC. Substrate and filter materials to enhance phosphorus removal in constructed wetlands treating diffuse farm runoff: a review. N Z J Agric Res. 2010;53:71-95.
[60] Johansson L. Industrial by-products and natural substrata as phosphorus sorbents. Environ Technol. 1999;20:309-316.
[61] Cui L, Zhu X, Ma M, Ouyang Y, Dong M, Zhu W, Luo S. Phosphorus sorption capacities and physicochemical properties of nine substrate materials for constructed wetland. Arch Environ Contam Toxicol. 2008;55:210-217.
[62] Wallenstein: report of lake in Casal de Cambra 2006; 2006.
[63] Douglas GB. Remediation material and remediation process for sediments. Patent CA2284766 C. 2002, p. 6.
[64] Lopes A. Estudo do Estado Trófico da Lagoa da Malagueira (Évora) e Proposta de Reabilitação. Deparatemento de Ciência e Engenharia do Ambiente, Universidade Nova de Lisboa; 2009.
[65] Plocher. Water Presentation, 2010.
[66] Asimov I. Asimov on chemistry. New York: Anchor Books; 1974.
[67] Council Directive 99/31/EC on the landfill of waste, 1999.
[68] Prud'homme. World phosphate rock flows, losses and uses. Phosphates 2010 International Conference, Phosphates 2010 International Conference, Brussels; 2010.